

The Correlation of Electrochromic Color Shifts with the Stoichiometric Parameters of Selected Copolymers and Polymer Blends

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Abstract

Three copolymers of N-vinylcarbazole and N-phenyl-2-(5'-vinyl-2'-thienyl)-5-(2''-thienyl)-pyrrole were synthesized using different feed stock ratios identical to the mass blends and characterized. Blends of poly(N-vinylcarbazole) (**PVK**) and poly(N-phenyl-2-(2'-thienyl)-5-(5''-vinyl-2''-thienyl)pyrrole) (**PSNPhS**) with similar compositions were prepared. Solid-state devices were fabricated, and the electrochromic properties of both systems were studied. In-situ spectroelectrochemistry and spectrophotometer measurements reveal that the electrochromic properties of these devices can be correlated with the ratio of the comonomers present. The observed color changes in the doped state of the devices were also correlated to the reflectance spectra.

INTRODUCTION

The ability to selectively adjust color contrast constitutes an important goal in the design of electrochromic devices. Organic materials can provide a wide range of colors resulting from variations in molecular structure.¹ The most versatile of these materials are the conjugated and non-conjugated polymers.² Among these materials, non-conjugated polymers containing pendant groups offer some advantages due to their distinct color contrasts and processibility.³ Although it would be unusual for a single conducting polymer to exhibit an electrochromic change encompassing the full visible spectrum,^{4,5} by using a combination of two polymers, each with distinctively different colors, a simple method of obtaining a wide range of colors might be achieved.^{6,7,8}

Previous work has shown that blends and copolymers can be used to modify the color of electrochromic devices.⁸ The precise color changes induced by these different methods of combining two polymers exhibiting different electrochromic properties remained undefined. To test this we chose two non-conjugated polymers containing pendant groups poly(N-vinylcarbazole), **PVK**,^{9,10} and poly(N-phenyl-2-(2'-thienyl)-5-(5''-vinyl-2''-thienyl)pyrrole), **PSNPhS**.⁸ In this paper we discuss the electrochromic color shifts resulting from three blends and three copolymers with similar ratios of **PVK** to **PSNPhS**.

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EXPERIMENTAL

Preparation of Electrochromic Devices:

Polymer blends were prepared by mixing different mass ratios of **PVK** and **PSNPhS** in chloroform. The compositions of various blends are as follows; **B1: PVK: PSNPhS (4:1)**; **B2: PVK: PSNPhS(2:3)**; **B3: PVK: PSNPhS(1:4)**. Copolymers were synthesized cationically using feed stock ratios of monomers identical to the mass ratios of the blends. The stoichiometries of the copolymers were estimated from the FT-IR spectra and are in fair agreement with the feed stock ratio. Data relating the composition of the copolymers and blends to the properties of the homopolymers are given in Table 1.

Table 1. Copolymer stoichiometry based on FT-IR spectra, absorption maxima in solution, and oxidation potentials of the copolymers and blends.

Polymer	Stoichiometry PVK:PSNPhS	λ_{max} (nm) CHCl ₃ Neutral	λ_{max} (nm) CHCl ₃ Doped	E _{ox} (V) vs Ag/Ag ⁺
PVK*	100:0	289, 340	480	1.1
B1	80:20	290, 340	480, 875	.63,1.1
C1	72:28	290, 334, 340	500, 900	.8
B2	60:40	290, 340	480, 875	.63,1.1
C2	61: 39	289, 334, 340	500, 900	.63
C3	30:70	289, 334, 340	495, 912	.63
B3	20:80	290, 320, 340	480, 875	.63,1.1
PSNPhS	0:100	289,340	490, 940	.60

* PVK was purchased from Aldrich Chemicals Inc.

Electrochemical studies

The voltammograms were collected using the Research Electrochemistry Software (version 4.0, EG&G Instruments Inc.) on an IBM-compatible 486 personal computer. The polymer was deposited onto the electrode (Pt or Altair OTM) by casting from a chloroform solution.

Spectroelectrochemical studies

Spectroelectrochemical measurements of the blends were recorded in 0.2M tetramethylammonium trifluoromethanesulfonate (TMATFMS) in acetonitrile in a specially modified quartz cuvette described previously.⁹ A cuvette containing a clean electrode in the electrolyte solution was used as reference. Spectra were recorded between 325-1200 nm as a function of incremental changes to the applied potential.

Device fabrication

Solutions containing polymers (2 ml at 4% w/v in chloroform) were repeatedly cast onto 15cm x 6cm ITO/Mylar strips (Altair OTM, Southwall Technologies, Inc.) using an Acculab Jr.TM 30 casting rod. The polymer films were air dried before assembling them into the device. The electrochromic material cast onto ITO serves as the anode in the electrochromic device. The blank ITO serves as cathode. A polymer electrolyte was prepared by mixing poly(methylmethacrylate) (M_w 120,000) (500 mg), propylene carbonate (1ml), ethylene carbonate (2 gm), and tetrabutylammonium tetrafluoroborate (300 mg) in acetonitrile (3ml) and was spun cast onto the blank ITO. The entire device was assembled in a sandwich composite (Figure 1).



The two pieces of mylar are put together face-to-face.

One edge of each piece hangs over the edge as an electrical contact.

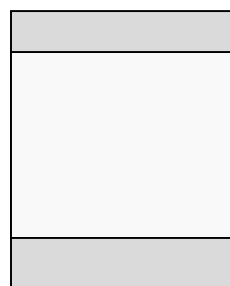
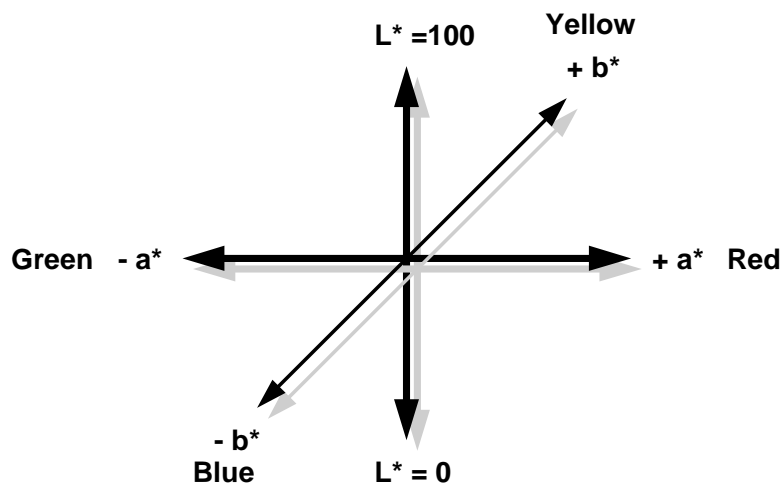


Figure 1. Typical solid state electrochromic device.

Reflectance and color measurements

The reflectance spectra and color measurements were performed on a Hunter Lab MiniScan XE spectrophotometer with the large view area option using a D65 Daylight illuminant. The MiniScan XE records the spectral reflectance over the visible range of 400 nm to 700 nm, with a resolution of 10 nm and a wavelength accuracy of 1 nm. The color data is displayed in CIE 1976 L*a*b* coordinates shown in Figure 2, using the CIE 1964 10 degree standard observer model.



Lab coordinate system

Figure 2. The Commission International de l'Eclairage L^* a^* b^* color coordinate system.

There is an inherent variability in thickness of polymer films within the devices which causes some variation in the CIE $L^*a^*b^*$ coordinates. Three devices composed from each blend and copolymer were constructed, and a series of doping/dedoping experiments were performed to reduce the effects in color measurements due to the variation in thickness. Typically, ten measurements were acquired and averaged for the doped and dedoped state of each device producing a standard deviation $\pm 2\%$ for each color coordinate measurement.

RESULTS AND DISCUSSION

The absorption spectra of the constituent homopolymer films are shown in Figure 3. The spectrum of the **PVK** homopolymer between 250 - 700 nm consists of three peaks at 290, 328, and 340 nm. The **PSNPhS** homopolymer has a broad absorption in the same region, with a peak maximum at 334 nm. The ratio of the areas under the peaks at 328 nm and 340 nm in the absorbance spectra of the neutral polymer blends and copolymers (Figure 4) correlates well with the ratios of the individual homopolymer components.

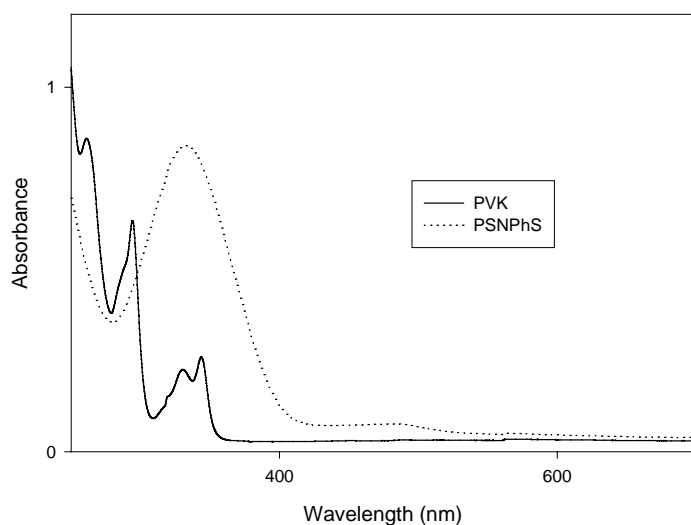


Figure 3. The absorption spectra of **PVK** and **PSNPhS** films.

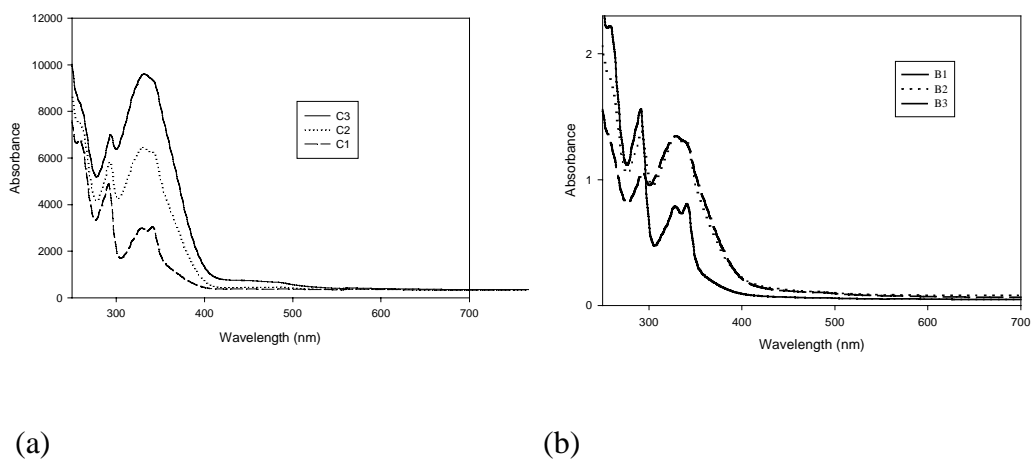


Figure 4. The absorption spectra of (a) copolymers and (b) blends of **PVK** and **PSNPhS**.

Spectroelectrochemistry

The spectral changes observed with an incremental increase in the potential for **B1** are shown in Figure 5. Two new peaks appear upon doping, one in the visible region at 480 nm and the second peak in the NIR region at 875 nm. The peak at 480 nm is ascribed to the absorption by radical cations of both species, whereas the peak at 875 nm may be due to the radical cations of

eight ring species formed upon cross-linking in case of **PSNPhS** and/or the carbazole diad in case of **PVK**.^{8,9,11} The broad nature of the absorption peaks suggests the overlap of the characteristic absorptions of both **PVK** and **PSNPhS**. The blends range in color from an olive green in the neutral state to a gray brown in the doped state.

Figure 6 shows the typical spectral changes upon doping these copolymers. Doping these copolymers leads to new peaks at 500 nm and 900 nm in the absorption spectrum with a distinct color change to the naked eye. All the copolymers appear to turn shades of brown in the doped state from their neutral pale yellow color. These peaks diminish upon dedoping and the copolymers regain the neutral color. The UV/Vis spectra of copolymers also show absorptions corresponding to the carbazole ring and the **SNPhS** moiety (Table 1).

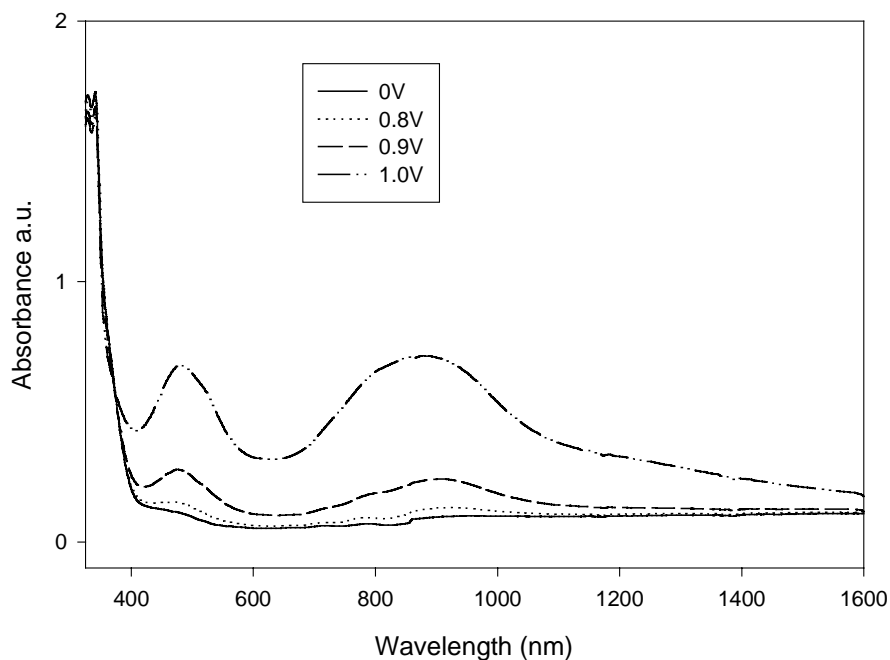


Figure 5. In situ spectroelectrochemistry of blend 1 (B1), which consists of 80% **PVK** and 20% **PSNPhS**.

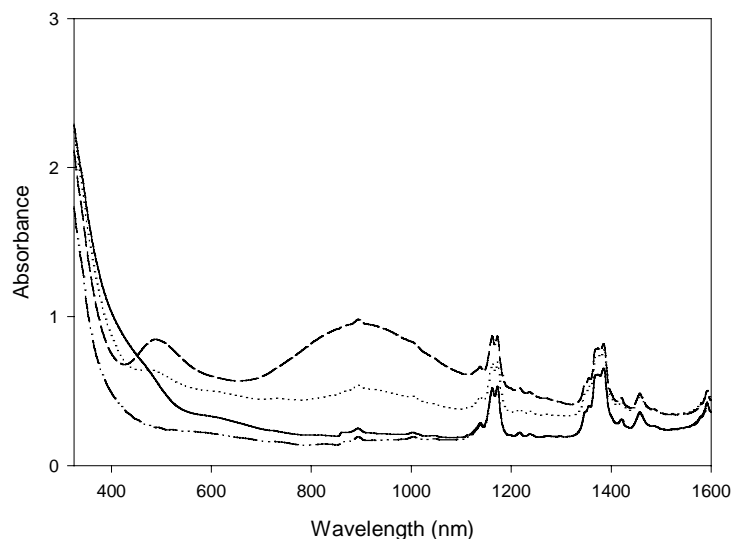


Figure 6. In-situ spectroelectrochemistry of copolymer C1.

Reflectance

Reflectance spectra provide another method to characterize these systems in the form of solid state devices. In the doped state, the homopolymers exhibit distinct difference spectra referenced to the dedoped states as in Figure 7.

Blends show a greater reflectance change in the 400-500 nm range while the difference spectra of copolymers indicate more change in the red portions of the spectra (600-700 nm). Figure 8 compared the difference spectra for reflected light from the copolymers and polymer blends referenced to the reflectance of their respective dedoped states.

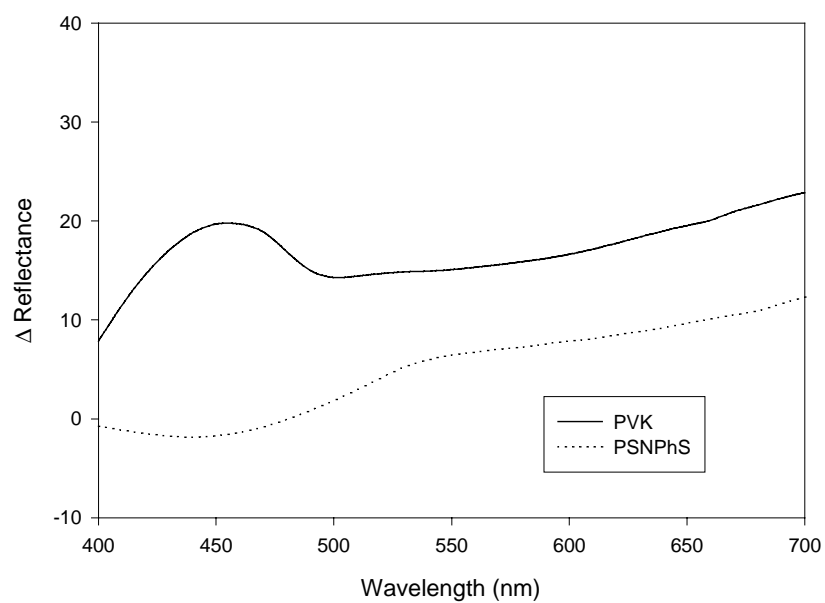
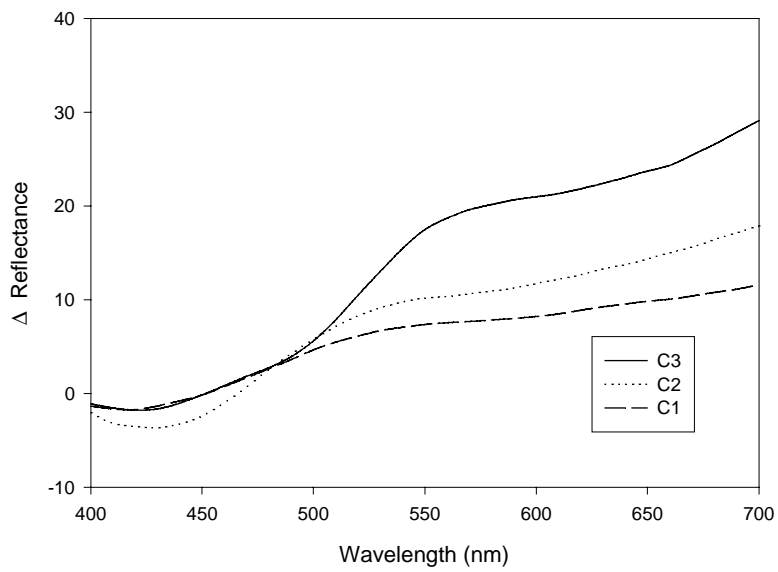


Figure 7. Difference spectra of reflectance in homopolymer reference to the dedoped state.



(a)

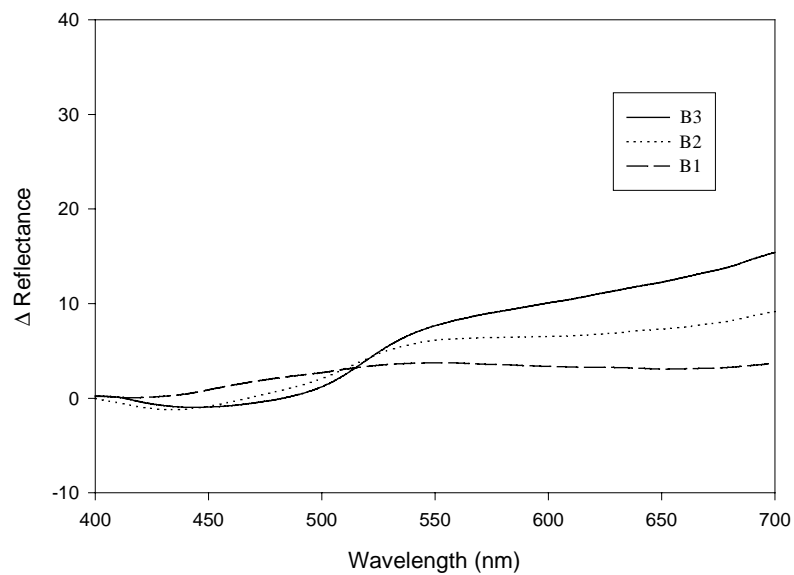


Figure 8. Difference spectra of visible light reflected from (a) copolymers and (b) polymer blends. The spectra are reference from the dedoped state of the solid state device.

Colorimetry

CIE 1976 $L^*a^*b^*$ coordinates for homopolymers and blends in the doped and dedoped states are given in Table 2. To the observer, the neutral state of **PVK** is colorless while **PSNPhS** is yellow; and while in the doped state, **PVK** is green and **PSNPhS** is gray-brown. The incremental change of the a^* and b^* coordinates in the doped state of these devices can be correlated to the amount of **PSNPhS** present. Data in Figure 9 indicate that the color of the doped polymer blend or copolymer is dependent on the amount of **PSNPhS** present.

Further analysis indicates that the red-green shift in the doped state of the copolymers and blends is strongly influenced by both homopolymers. In the doped state, the a^* values show a correlation ($R^2 = 0.9403$) with the **PSNPhS** quantity in the blend shown by the regression curve in Figure 10. Such an increase of a^* and b^* in the doped state qualitatively indicates a color change towards orange (yellow and red mixture) on the $L^*a^*b^*$ scale.

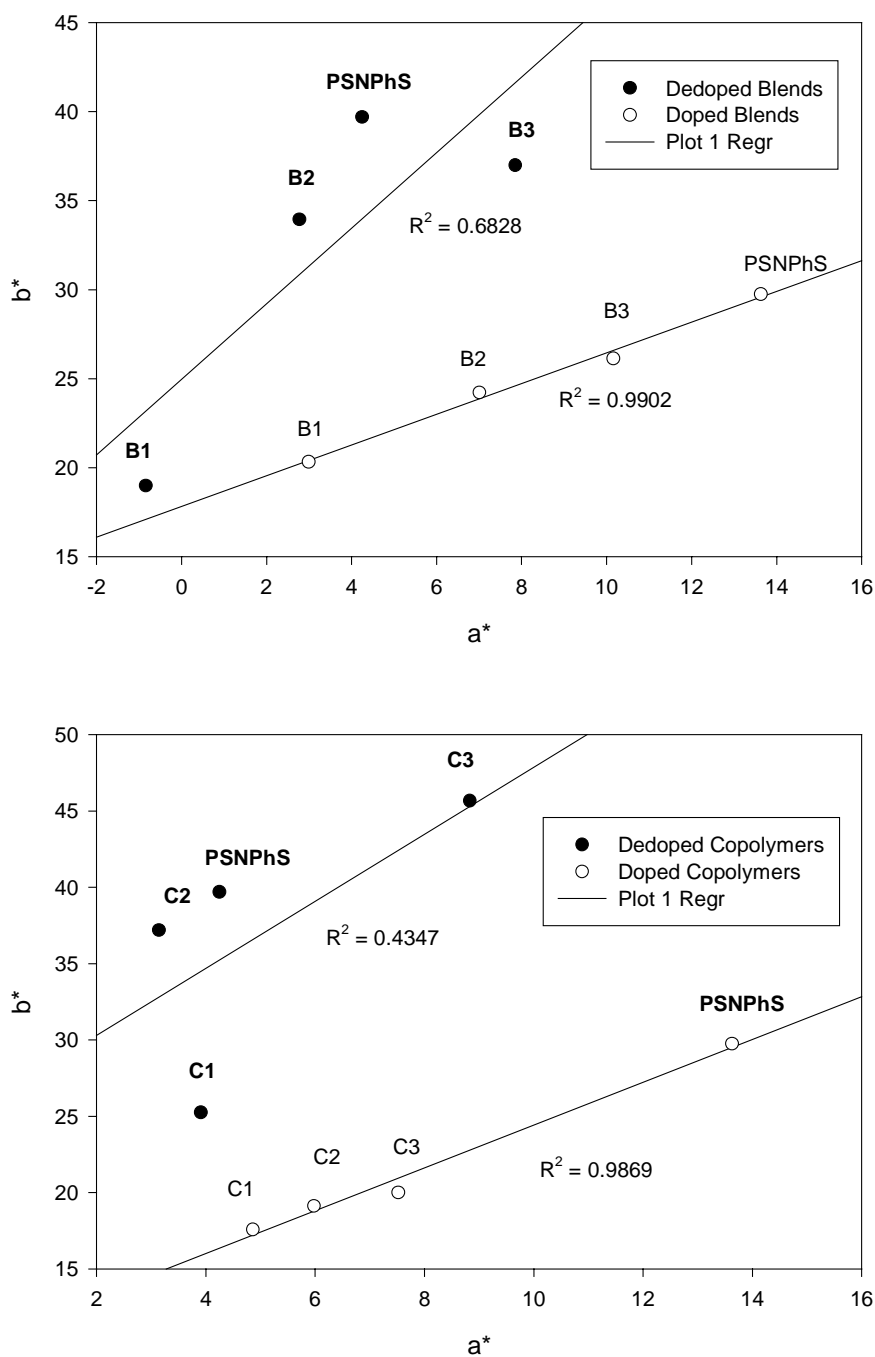
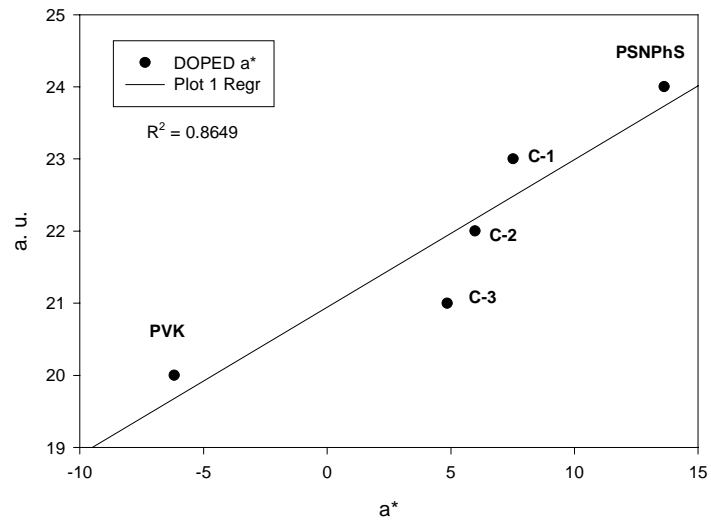


Figure 9. Correlation of the a^* and b^* values for the doped and undoped states of blends and copolymers as a function of **PSNPhS** content.

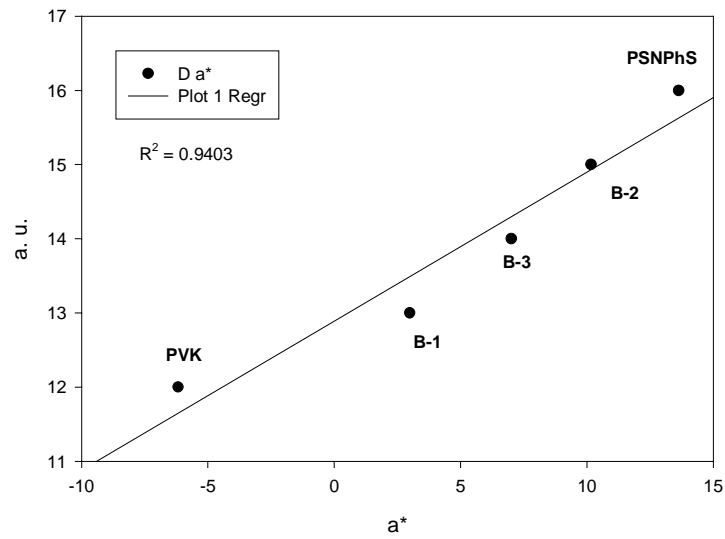
Table 2. CIE 1976 L* a* b* coordinates for homopolymers and polymer blends in a doped and dedoped state

Polymer	Dedoped			Doped		
	L*	a*	b*	L*	a*	b*
PVK	83.86	-2.31	18.72	78.43	-6.18	27.17
B1	83.16	-0.84	18.99	76.55	2.99	20.33
C1	71.88	3.91	25.25	67.08	4.86	17.58
B2	75.46	2.77	33.94	69.63	7.01	24.22
C2	71.95	3.14	37.19	61.17	5.98	19.12
C3	62.44	8.83	45.67	46.69	7.52	20.00
B3	62.75	7.85	36.98	55.42	10.16	26.13
PSNPhS	68.80	4.25	39.69	64.58	13.63	29.75

The observed change in the L* a* b* values from Table 2 can be correlated to the copolymer composition. The a* value, which is a measure of red component, decreases with decreasing the amount of **SNPhS**. This trend is readily seen from Figure 9 which shows the change in a* value with respect to b* for all three copolymers. Similarly, the reflectance spectra also show this trend.



(1)



(2)

Figure 10. The regression of CIE coordinate a^* for (1) homopolymers and polymer blends in the doped state, and (2) The regression of CIE coordinate a^* for homopolymers and copolymers.

CONCLUSIONS

It is possible to adjust the electrochromic color contrast of solid-state devices by controlled stoichiometric application of two different polymers combined as copolymers or as blends. The type of variation in the color as measured by CIE L^* a^* b^* coordinates depends on the method of combination. Note that the color contrast observed in copolymers is different from the color contrast observed in the homopolymer blends based on the individual monomers. In the case of **PVK** and **PSNPhS**, it appears that copolymer combinations allow tailoring of the b^* coordinate (Blue-Yellow) component of the color contrast, while stoichiometric adjustments in the blends of these polymers correlate well to changes in the a^* coordinate (Red-Green).

This study shows the correlation between the stoichiometries of these copolymers, polymer blends, and their electrochromic color properties. Such strategies could be used to fine-tune electrochromic color properties in the desired manner. Although there have been numerous reports on achieving tailor-made color, we believe that the present technique of tailoring color by varying the stoichiometry in copolymers and polymer blends is simple and effective.

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